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COMPLETE SPECIFICATION

Zirconia Rods for Coating Articles by Flame Spraying

We, NORTON GRINDING WHEEL COMPANY LIMITED, of Welwyn Garden City, Hertfordshire, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to zirconia rods for coating articles by flame spraying.

One object of the invention is to provide zirconia rods which will ensure uniform coatings on articles by the flame spraying process described in British Patent No. 745,257. Another object of the invention is to provide superior zirconia rods for use in the process, which do not cause spitting.

Another object is to make rods for this flame spraying process which have greater thermal shock resistance and which will melt readily without spalling. Another object is to eliminate fracturing of such rods during flame spraying and thus avoid the ejection of considerable lengths of white hot rods from the gun.

We have discovered that a coarse grained rod sprays uniformly in the gun and is superior to a fine grained dense rod even though the strength of the fine grained dense rod is greater. For example, when a zirconium oxide rod is made from a mixture of 325 mesh and finer fused stabilized zirconia, extruded and fired to cone 35 Orton, a very strong, dense finely crystalline rod is obtained. Such a rod can be used for flame spraying but pieces of the rod which have not melted often break off and are projected by the compressed air blast onto the surface being coated. Such pieces may stick to the surface and cause a defect in the coating, or they may bounce off in which case they become hazards to people and property. The rate of feed of the rod and thus the spraying rate must also be kept low in order to use these dense rods. Even then this breaking off of pieces of rod (sometimes called spitting) will occur.

The invention consists in a sintered zirconia rod for flame spraying to coat articles with zirconia, comprising zirconia the majority of the crystals of which are cubic and tetragonal, having a porosity of 8% to 40% by volume of voids constituted by open and interconnected pores, said rod having a breaking stress of more than 2,000 pounds per square inch and apart from hafnia, and lime, magnesia, ceria or titanium monoxide used for stabilizing the zirconia being at least 96% pure zirconia.

In each of the following examples 1 and 2 the material consisted of zirconia particles 30% by weight of which are coarser than 100 microns and substantially all of which are finer than 500 microns.

The preferred formula for the zirconia rods according to our invention is given in the following table:

TABLE I

Material	Percent by Weight
Fused stabilized zirconia 90F grit size. 90 grit size is 216 microns size. This is ZrO_2 which has been fused in the electric furnace having from 3% to 6% of lime, CaO, in accordance with U.S. patent to Ballard and Marshall, No. 2,535,526, granted December 26, 1950. The preferred variety which we use contains 5% of lime.	75
The same fused stabilized zirconia 90% of which is from 25 to 50 microns in size.	15
Fused unstabilized zirconia having no added lime 90% of which is 25 to 50 microns in size.	10

The designation F after a number, which indicates the size of a screen in openings per linear inch, means that an under screen is not used and 75% of the material is finer than the indicated size down to impalpable fines.

EXAMPLE I

100 weight parts of the material of Table I is mixed with 17 weight parts of water, 1 weight part of dextrine, and 2 weight parts of corn starch to produce the desired porosity. After thorough mixing the resultant mixture is extruded thus forming rods, which are either one eighth of an inch in diameter or three sixteenths of an inch in diameter. An allowance of 3% of the diameter is made for shrinkage during firing. The rods are then dried by passing hot air over them and after drying they are fired by placing them in a kiln heated to cone 35 Orton. The rods are then ready to be used in the spraying process described in our Patent No. 745,257.

Another formula which can be used according to our invention is given in the following table:

TABLE II

Material	Percent by Weight
Fused stabilized zirconia (as in Table I) with an average size of 200 microns.	54
Stabilized zirconia (as in Table I) with a size of 50 microns and finer.	46

EXAMPLE II

100 weight parts of the material of Table II is mixed with 18 parts of water, 1 weight part of dextrine and 2 weight parts of corn starch. The rest of the procedure is the same as for example I.

In accordance with our invention, other materials may be used in the mixture which will burn out and leave pores in the rod where the material has burned out. Such material can be sawdust, walnut shells, coffee, or organic resins. Pores can also be introduced by materials which sublime such as paradichlorobenzene. With the pores artificially introduced in this manner, the size of the zirconia powder used can be similar to that of our preferred composition or it can be a very fine powder. Such a formula for producing a porous rod with fine stabilized zirconia powder is given in the following table:

TABLE III

Material	Percent by Weight
Stabilized zirconia (as in Table I) with a size of 25 microns and finer.	90
Nut shells, 175 to 225 microns.	10

EXAMPLE III

100 weight parts of the material of Table III is mixed with 20 weight parts of water, 1 weight part of dextrine, and 3 weight parts of corn starch. After thorough mixing the mixture is extruded thus forming rods. An allowance of 17% of the diameter is made for firing shrinkage when fired to cone 35. Since fine particles will sinter more readily, satisfactory rods of this mixture can be made by firing only to cone 14, but we prefer to fire them to cone 35 to make them stronger, so that they are easier to handle.

Rods according to our invention, besides being sintered zirconia rods, have crystals the majority of which are cubic and tetragonal. The reason for this is that when zirconia is either cubic or tetragonal, it has strong resistance to heat shock and we find that rods for flame spraying should have this property. Furthermore, the coating is preferably resistant to heat shock which is another reason for having the majority of crystals cubic and tetragonal. The firing of the rods sinters the particles together and the rods are therefore said to be sintered rods.

Zirconia having at room temperature all cubic crystals is fully stabilized and so is zirconia with all tetragonal crystals but within the scope of this invention, for many practical uses, a partially stabilized zirconia having up to 50% of monoclinic crystals (at room temperature can be tolerated. One way of stabilizing zirconia is by fusing it with lime in accordance with the disclosure of the patent mentioned in Table I. There are other ways of stabilizing zirconia, such as by fusing it with magnesia or with cerium oxide or with titanium monoxide, in varying proportions, but our invention is better defined by stating the crystal habit. When monoclinic crystals are heated to a certain temperature there is a sharp volume change which produces fractures on subsequent cooling, but this phenomenon is either absent or not so pronounced when the majority of the crystals are, originally, of the cubic or the tetragonal variety. In the foregoing examples the stabilized zirconia contains more than 55% of cubic and tetragonal crystals and the porosity of the products is 8% to 40% by volume. The breaking stress exceeds 2000 pounds per square inch.

All commercial zirconia used up to this time, with the exception of some for special purposes, has a minor content of hafnia, HfO_2. However, hafnia reacts chemically or fails to react with almost all other materials in the same way as zirconia. Furthermore, the hafnia content of zirconia is, except for certain special uses, referred to as zirconia. Therefore, our rods are herein referred to as zirconia rods although they usually will have a minor portion of hafnia. However the only detriment in the use of zirconia without hafnia is that it is expensive.

Our rods resist spitting and are superior to prior rods since they have a porosity of from 8% to 40% by volume percent void constituted by open interconnecting pores. These pores cut down the thermal conductivity which can lead to fracture and spitting. Rods according to our invention are not so strong as those heretofore existing but, and this surprising, they are quite superior to the latter for flame spraying. They have a minimum strength and they are satisfactory as they have a breaking stress of more than 2,000 pounds per square inch. Our rods are, apart from the hafnia content and apart from the oxide used for stabilizing the zirconia, contain at least 96% pure zirconia.

Suitable firing conditions may be from cone 20 to cone 42 Orton, but we prefer to fire the rods under cone 35 Orton conditions or thereabouts. In general, the higher firing temperatures produce stronger rods, but will also decrease the porosity, and furthermore, attaining the higher firing temperature is expensive.

In stating that the zirconia apart from its hafnia content and the stabilizing oxide content is at least 96% pure zirconia, we have in mind that a minor proportion of iron oxide, say 1%, a small proportion of silica, say 2%, and a minor proportion of titania, say 1% will not be so detrimental as to make an inferior rod for purposes of flame spraying. There might be other contaminants in the zirconia, provided all of them together do not exceed 4% of the ZrO_2. The hafnia and the stabilizing oxide are of course not contaminants the former being completely compatible with the zirconia and the latter greatly improving it. We prefer to have in most cases as small amount of the contaminants as possible but some contamination cannot be avoided, as is the case with most compounds.

When used in flame spraying equipment, a rod is brought to the melting point at the tip in the flame, and a very high temperature differential is established between the molten end and the cool portion of the rod. This temperature differential causes differential expansion and thus high stresses near the molten tip of the rod. The dense, homogeneous, fine grained, strong rods break from these high thermal stresses. Small pieces shear off before they become molten, and are projected as solid particles rather than molten drops. These solid particles produce defects in the coating.

When the rod is coarsed grained, it is more porous and has a lower mechanical strength. Fired dense zirconia rods have a breaking stress of 16,000 pounds per square inch, while fired rods of the preferred composition shown in Table I have a breaking stress of 8,000 pounds per square inch. These values were measured on $\frac{1}{8}''$ diameter rods which were supported on a 5″ span, and loaded in cross-bending at the centre of the span. The bulk density of the dense rod is 5.2 grams per cubic centimeter while the bulk density of the preferred rod of Table I is 4.3 grams per cubic

centimeter. The theoretical density of zirconia, ZrO_2, is 5.7 grams per cubic centimeter. All rods made according to the foregoing examples contain pores of which more than 50 volume percent are more than 20 microns in diameter.

WHAT WE CLAIM IS:—

1. A sintered zirconia rod for flame spraying to coat articles with zirconia, comprising zirconia the majority of the crystals of which are cubic and tetragonal, having a porosity of 8% to 40% by volume of voids constituted by open and interconnected pores, said rod having a breaking stress of more than 2,000 pounds per square inch and apart from hafnia and lime, magnesia, ceria or titanium monoxide used for stabilizing the zirconia being at least 96% pure zirconia.

2. A sintered zirconia rod according to claim 1, said rod having been made out f zirconia particles thirty percent by weight of which are coarser than 100 microns and substantially all of which are finer than 500 mircons.

3. A sintered zirconia rod according to claim 1 or claim 2, said rod having been fired under from cone 20 to cone 42 Orton and preferably cone 35 Orton firing conditions.

4. A sintered zirconia rod according to any one of claims 1, 2 or 3 containing pores of which more than 50 volume percent are more than 20 microns in diameter.

5. Sintered rods of zirconia according to any preceding claim, when prepared in accordance with any of the foregoing examples.

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